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APPLICATION NUMBER: *60/441,743*
FILING DATE: *January 21, 2003*
RELATED PCT APPLICATION NUMBER: *PCT/US04/01696*

Certified by

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01-23-03 60441743 012103 APP-OV- $

PTO/SB/16 (10-01)
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EU400563395US

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☐ Additional inventors are being named on the ____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

NANOPARTICLE-COATED NANOSTRUCTURED SURFACES FOR DETECTION, CATALYSIS, AND DEVICE APPLICATIONS

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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification *Number of Pages* 16 ☐ CD(s), Number

☒ Drawing(s) *Number of Sheets* 13 ☐ Other (specify)

☐ Application Data Sheet. See 37 CRF 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant claims small entity status. See 37 CFR 1.27

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FILING FEE AMOUNT ($): $80

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

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Respectfully submitted,

SIGNATURE L Jones

Date January 21, 2003

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REGISTRATION NO. (if appropriate)

TELEPHONE (814) 238-4926

Docket Number: 2002-2733

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

Practitioner's Docket No.: 2002-2733 **PATENT**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: A. Kalkan, et al.
Serial No.: Group No.:
Filed: January 21, 2003 Examiner:
For: NANOPARTICLE-COATED NANOSTRUCTURED SURFACES FOR DETECTION, CATALYSIS, AND DEVICE APPLICATIONS

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NANOPARTICLE-COATED NANOSTRUCTURED SURFACES FOR DETECTION, CATALYSIS, AND DEVICE APPLICATIONS

By: Ali Kaan Kalkan
Stephen J. Fonash

BACKGROUND OF THE INVENTION

SPR spectroscopy has been extensively used to monitor a broad range of analyte-surface binding interactions including the adsorption of small molecules, ligand-receptor binding, protein adsorption, antibody-antigen binding, DNA and RNA hybridization and protein-DNA interactions. The sensing mechanism of SPR spectroscopy is a shift in SPR energy of a noble metal nanoparticle in response to a change in refractive index of its surroundings due to analyte binding at or near its surface. The refractive index sensitivity of SPR biosensors and chemosensors has been reported to be on the order of 1 part in 10^5–10^6 corresponding to an areal mass sensitivity of 10–1 pg/mm^2.

Metal (e.g., Ag, Au and Cu) nanoparticles can exhibit a strong optical absorption and reflectance in the UV-vis range of the electromagnetic spectrum that is not present in the spectrum of the bulk metal. When the particle size is much smaller than the wavelength of the incident electromagnetic radiation, the electrons in the particle move in phase, that is, they generate a giant oscillating dipole (or multipole depending on the shape of the particle). Collective motion of the electrons generates surface polarization charges on each side of the particle, which act as a restoring force on these electrons. Because of the restoring force a resonance condition occurs at a certain frequency at which the amplitude of the oscillating dipole can be excited to a maximum.

These collective electron oscillation modes that can be excited by electromagnetic radiation (photons) are termed particle plasmons, localized surface plasmons or simply surface plasmons (plasmons can also be excited by high energy electron collisions). The associated absorption of the electromagnetic energy (photons) for the generation of these collective electron oscillation modes is seen as a band in the optical absorption spectrum and is called the surface plasmon absorption band. It is well established that plasmon energy of particles (e.g., the wavelength or frequency of the surface plasmon absorption peak) is dependent upon size, shape, and interparticle spacing as well as on particle and local environment dielectric properties. When the particle size increases (or when nanoparticles aggregate so electrons can travel from one nanoparticle to another) electrons become dephased and they cannot generate a strong restoring force. Consequently, the plasmon absorption band broadens and gets weaker.

Metal nanoparticles also exhibit interesting electronic, magnetic and catalytic properties that are not present in the bulk metal. These unique properties of nanoparticles are tunable by

varying particle size, shape and spacing. For example, colloidal suspensions of gold can be red, purple, or blue, depending on the size, spacing and environment of the gold particles. In addition, gold clusters on a titania surface have been shown to yield catalytic oxidation of carbon monoxide that becomes most effective when the cluster diameter is reduced to ~3 nm. Hence, metal nanoparticles or nanostructured metal surfaces with their unique properties and enhanced surface area offer exciting opportunities for the development of novel sensors and catalysts, etc.

The most common and simple approach to the synthesis of metal nanoparticles is through colloidal chemistry. This method involves a precipitation reaction in a liquid solution to form the nanoparticles; however, the particles may aggregate unless an appropriate surfactant is used. On the other hand the surfactant may hinder certain sensing mechanisms. An alternative approach uses the patterning of continuous metal films by electron beam lithography to form nanoparticles immobilized on a substrate with precise control of size, separation and shape. However, this technique involves high costs, low throughput and is limited to a minimum particle size of ~10 nm. Metal nanoparticles can alternatively be obtained by condensation of a metal vapor on a substrate surface in the form of islands. Although vapor deposition is a lower cost and higher throughput process than electron beam lithography, control of particle size and spacing is difficult.

DETAILED DESCRIPTION OF THE INVENTION

In Provisional Patent Application No. 60/402,173, the present inventors disclose a novel non-vacuum-based method of synthesizing metal nanoparticles. The application reveals that nanoparticles of certain metals (e.g., Au, Ag and Cu) can be controllably synthesized on the surfaces of nanostructured void-column Si films simply by exposure of the void-column material to the salt solutions of said metals. These composite nanoparticle/void-column film substrates have been found to yield strong surface plasmon optical absorption and surface enhanced Raman scattering (SERS). Since the inventors' approach does not require any electric power, reducing agents, heating, or catalysts to form the metal nanoparticles, it is very attractive. This metal deposition reaction is attributed to galvanic displacement, where the film surface itself serves as the reducing agent and electron source for reduction of the metal salt. However, such reaction was shown to proceed on Si surface only in the presence of HF. This is because the metal salt is reduced in the expense of oxidation of Si. In other words, Si-Si bonds break and supply the electrons used to reduce the metal salt on the Si surface, leading to subsequent oxidation of the Si

surface by the ambient. The oxide is a dielectric and impedes the electron transfer. Therefore HF is required to remove the oxide so that electron transfer can be maintained and metal deposition can occur. On the other hand, in the present invention no HF is necessary for metal coating to occur.

It is likely that a different condition is enabled by the nanostructured surfacc of the present invention such as electron tunneling through the oxide or dissolution of oxide by the metal salt solution. Furthermore, metal nanoparticle formation on the void-column film was observed to persist upon oxide passivation, at a lower rate, or dehydrogenation of the nanostructured Si surface.

Provisional Patent Application No. 60/402,173 describes the use of the present invention to fabricate SERS substrates for molecular detection. The present disclosure describes additional novel and inventive steps based on this approach (e.g., surface plasmon resonance (SPR) sensors and nanocatalysts).

The nanostructured void-column Si films (interconnected void network material) cmployed in this invention were deposited on Corning 1737 glass substrates using a high density plasma deposition tool (PlasmaTherm SLR 770 ECR-PECVD system). Table I lists the film deposition conditions: SiF_4 was incorporated during the deposition process. The impact of SiF_4 use was enhancement of columnar separation along with avoidance of columnar aggregation; hence, a gain was achieved in accessible inner surface area (for subsequent metal nanoparticle adsorption or attachment). Accordingly, all experimental data presented hcre were derived using films deposited as in Table I, although electroless synthcsis of metal nanoparticles was also found to occur with films grown as described in references 10 and 11.

Fig. 1 shows a plain micrograph of a typical nanostructured void column Si film deposited as in Table I. An array of 20-30 nm wide nanocolumns with an average separation of 20 nm is seen comprising a high surface to volume ratio material. As evidenced from detached nanocolumns (i.e., separated from the substrate) lying on the film surface, the shape of the columns is rod-like (nanorods). Unless otherwise stated the films used for this demonstration were grown to a thickness of 2000 Å.

Fig. 2 depicts time evolution of optical absorbance of void-column Si films immersed in 0.001 M Ag_2SO_4 solution. A systematic increase in absorption with time in the violet-blue region is seen. This translates to the naked eye as a gradual transition from lighter brown to

darker brown (transmission). Spectra in Fig. 3 were derived from those in Fig. 2 by subtracting each spectrum from that of unexposed film in order to isolate the effect of deposited Ag from that of Si film and substrate alone. The absorption band peaking at ~3.0 eV is characteristic of surface plasmon resonance associated with Ag nanospheres. This implies that Ag deposition occurs in the form of spherical nanoparticles.

The fact that only the absorption band increases in intensity while its peak persists at the same energy with prolonged exposure implies an increase in particle density with the average particle size remaining the same. This interesting feature may be related to the average columnar separation, which remains unchanged during the emersion exposures, thereby limiting the particle size. This result also implies that there is no particle aggregation and there is sufficiently large interparticle spacing such that particles are weakly or not electromagnetically coupled.

One may anticipate that metal particle nucleation would only take place on the top surface of the Si film. However, as evidenced from Fig. 4, this is not true. Surface plasmon absorbance is clearly seen to increase with film thickness. Hence, Ag nanoparticles must also nucleate inside the film, possibly on the lateral surface of Si nanocolumns (throughout the film thickness). In other words, the increase in plasmon absorption with Si film thickness implies that Ag particles are synthesized throughout the thickness of the Si film in a three-dimensional ("3-D") array fashion. Indeed, as seen in Fig. 5, a scanning electron microscope study confirms the presence of monodispersed Ag particles spaced uniformly along Si nanocolumns whose average size is on the order of columnar spacing. Therefore, the nanostructured Si films not only enable easy synthesis of 3-D arrays of Ag nanoparticles, but also enable monodispersion and narrow size distribution of the nanoparticles without the use of a surfactant.

The interconnected or continuous void volume of the nanostructured Si plays an essential role in the formation of three-dimensional nanoparticle arrays. The interconnected or continuous void network feature of the void column Si films enables the metal salt solution to reach and occupy the entire void volume, thereby enabling the synthesis of nanoparticles throughout the three-dimensional void network.

Scanning electron microscope (SEM) micrographs of the top film surface for various exposure times are shown in Fig. 6. The improved clarity with increased exposure time is attributed to increased conductivity of the films with increased Ag deposition which helps to reduce SEM charging effects. Ag nanospheres of various sizes are clearly seen on the surface of

90 s exposed film. Since there is no constraint on particle size on the top surface of the film, Ag nanoparticles occupying that position on the void-column film may, with additional exposure, grow to the order of the wavelength of light in the visible range. This can lead to bulk-like metallic reflectance emerging with enough emersion time.

Fig. 7 shows the reflectance of the void-column Si film that was coated with Ag nanoparticles for 50 s in the 0.001 M Ag_2SO_4 solution. The reflectance spectrum of an as deposited void-column Si film is also plotted. The reflectance spectrum shows interference peaks that decay as energy increases. The pronounced reflectance band that emerges is due to the presence of Ag nanoparticles and is of about the same peak location and width as the plasmon absorbtion band (also shown in Fig. 7). Hence, the trends in reflection mimic those in absorption. This is because scattering is strongest when the induced dipole is largest, coinciding roughly with the surface plasmon resonance. Therefore, sensors based upon surface plasmon resonance in reflectance mode can also be designed.

Fig. 8 shows surface plasmon absorption bands of Au nanoparticles synthesized on the surface of a void-column Si film immersed in a commercial Au electroplating solution (diluted to 1:5 in H_2O) for various times (obtained from Technic Inc., RI, with specification Techni Gold 25). The absorbtion peak at ~2.3 eV is due to surface plasmon resonance in Au nanospheres.

Figs. 9, 10 and 11 demonstrate three SPR sensors fabricated from Ag/Au nanoparticle coated void-column Si films. The analyte molecule is methyl sulfoxide, which was spun on the films (sensors) at 1000 rpm, for 20 s. For both Ag and Au, the red shift of the plasmon band is a response to the adsorption of methylsulfoxide.

As previously mentioned, SPR spectroscopy is a well-known tool for fabricating arrays of noble metal nanoparticles on foreign substrates (for the demonstration of SPR sensors). To the inventors' knowledge, the present technique is the only technique that describes a method of producing such nanoparticles without need for lithography, catalysts, electrical current, or vacuum deposition on a nanostructured surface. The present invention also demonstrates the effectiveness of the system for SPR sensing. Besides its remarkable simplicity and speed in the synthesis of nanoparticles, the present approach is associated with higher sensitivity by virtue of the enhanced surface area provided by the void-column morphology (interconnected void network) available for nanoparticles as well as analyte molecules.

The surface plasmon resonance can be made stronger by increasing the number of metal nanoparticles per unit area of the substrate and by increasing the void-column film thickness (as shown in Fig. 4) without changing the average spacing between particles. In other words, the present approach results in a 3-D array of nanoparticles rather than a 2-D array, with a higher areal density of nanoparticles for a given interparticle spacing. Therefore, sufficiently large interparticle spacing can be maintained with weak electromagnetic coupling between particles, yet a high signal to noise ratio can still be obtained with a high number of nanoparticles per unit area. Furthermore, void-column morphology also enables dramatically enhanced sensing of vapors by means of capillary condensation in the voids, since the analyte is expected to yield a much higher surface plasmon shift in liquid phase than in vapor phase.

The present approach of synthesizing nanoparticles on nanostructured surfaces by immersion in chemical solutions can also be used to obtain nanoparticle-based catalysts where the synthesized nanoparticles are supported on a high surface area (e.g., porous) substrate. In fact, many industrial catalysts are comprised of nanoparticles dispersed on a support.

The key advantages of utilizing nanoparticles as catalysts are: 1) catalytic activity can be dramatically enhanced and tuned by the shape and size of the nanoparticles (or futures of the structure) resulting in lower reaction temperatures and faster reaction rates; 2) selectivity can be tuned by the size and shape of the nanoparticles; 3) extreme enhancements in surface area can lead to enhanced yield; and 4) nanoparticle regeneration may occur. These advantages help decrease pollution, raw material and energy consumption, and enhance yield.

Catalytic activity is known to be high at edges and kinks. The higher free energy at strained, broken bonds helps surmount the activation barrier. In general, catalytic activity increases with decreasing particle/feature size as the reduced radius of curvature leads to more strained and/or unsatisfied bonds at the surface. Scanning tunneling microscope (STM) images of catalyst nanoparticles show the presence of different electron states on the surface of the nanoparticles. These surfaces differ from regular (bulk) surfaces. Quantum confinement modified electron states below the surface may also play a role in catalytic activity. Quantum confinement alters density of electron state distribution. In severe confinement, workfunction or Fermi level (electrochemical potential) changes and discrete (atomic like) states can emerge above and below the conduction band. This has a huge impact on electron transfer across the surface during a chemical reaction. Recent work has shown that smaller is not necessarily better.

In general, catalytic activity increases with decreasing size down to approximately 1-3 nm. However, catalytic activity starts to decrease below a critical size. Hence, a resonance condition is implied that depends on the energy distribution of electron states.

In Provisional Patent Application No. 60/402,173, the present inventors demonstrated that nanostructured Si surfaces coated with metal nanoparticles can serve as surface enhanced Raman scattering (SERS) active substrates. Fig. 12 of the present invention further exemplifies SERS activity of a nanostructured void-column Si film coated with Ag nanoparticles. In the demonstration, the analyte molecule was applied as 1.0 μL of solution on the Ag nanoparticle coated film which was subsequently left to dry. A laser beam was directed at the center of the spot where the 1.0 μL analyte solution droplet had dried. In general, for analyte concentrations higher than 10^{-7} M, the analyte spot is visible to the naked eye in the form of a circular stain after the droplet dries. Measurements may also take place in the wet state before the solution dries using an immersion lens.

In addition, alternative means of applying the analyte molecule(s) to the nanoparticle-coated surface may be employed. These include spinning, spraying, inkjet/robotic printing from a solution, and diffusion or convection from the gas/vapor or plasma phase. A different approach involves applying a mixture of the metal salt solution and the analyte solution to the virgin nanostructured film surface (uncoated with metal nanoparticles). In this approach, the metal nanoparticles are only synthesized where the solution mixture is applied and within the time that the droplet dries. Hence, synthesis of metal nanoparticles and attachment of analyte molecules on them occur simultaneously. This minimizes the exposure of the metal particle surface to ambient before analyte is adsorbed on it. As a result, background noise due to contaminants like hydrocarbons is reduced.

In SERS, the enhancement in Raman signal is principally attributed to enhanced electric fields in the neighborhood of metal particles. Once the surface plasmon modes (collective oscillations of free electrons) in a metal nanoparticle are in resonance with the impinging electromagnetic field such as an impinging laser beam, high oscillating dipoles are induced in the nanoparticle that in turn develop strong local electric fields in their vicinity. The amplitude of the local electric field decays exponentially along the nanoparticle surface normal with a characteristic decay length of 5-6 nm or a saturation distance of ~30 nm. This amplification in local electric field is for both incident light and Raman scattered light. As a result, enormous

gains are possible in the intensity of the SERS signal that is the fingerprint of the adsorbed molecule.

These local field enhancements can also lead to enhancements in other transitional phenomena such as optical absorption, reflectance, fluorescence, ionization, field emission, charge separation, and stimulated emission etc. upon which novel sensors and devices can be based. For example, Lacowicz et al. have recently shown that intrinsic fluorescence from DNA can be enhanced 80-fold in the presence of Ag nanoparticles. On the other hand, Fig. 13 depicts enhancement of optical absorption in rhodamine when it is coated on the Ag nanoparticle deposited nanostructured Si surface of the present invention. Furthermore, such enhanced local fields can be employed to enhance the rate of certain photochemical reactions.

Figure 3 indicates that plasmon absorption associated with Ag nanoparticles disposed on a nanostructured void column Si surface can be controllably increased by prolonging immersion time. For the 80 s sample, the optical absorbance is seen to be above 2 at 3 eV, which corresponds to an optical transmission of less than 0.01. Hence, almost complete coupling of the electromagnetic (optical) energy to plasmon modes occurs. Therefore, the nanoparticle coated nanostructured surfaces described herein may be utilized in photonics to couple light from one system to another. Furthermore, such material compostions in thin film form may serve as anti-reflection coatings.

Finally, nanoparticles of varying density may be selectively patterned on the nanostructured surface by employing a technique such as dip pen lithography. In this way, optical and magnetic information storage systems can be built.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various alterations in form and detail may be made therein without departing from the spirit and scope of the invention.

TABLE I. Process parameters employed in PlasmaTherm SLR 770 ECR-PECVD system to deposit void-column Si films.

Upper magnet current	173 A
Lower magnet current	24 A
Substrate temperature	100 °C
Incident microwave power	400 W
Reflected microwave power	50 W
Process pressure	10 mTorr
SiH_4 flow rate	1.5 sccm
SiF_4 flow rate	0.7 sccm
H_2 flow rate	40 sccm

PREFERRED EMBODIMENTS

Examples of the preferred embodiments of the invention include:

1. A nanoparticle-nanostructured material composite comprising:

a) a nanostructured material; and

b) generally uniform nanoparticles disposed on a surface of the nanostructured material.

2. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a size range capable of producing enhanced local fields when excited externally.

3. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanostructured material comprises a high surface to volume ratio.

4. The nanoparticle-nanostructured material composite of embodiment 3, wherein said high surface to volume ratio material comprises a continuous void network.

5. The nanoparticle-nanostructured material composite of embodiment 4, wherein said continuous void network material comprises a column-void material.

6. The nanoparticle-nanostructured material composite of embodiment 2, wherein said external excitation is electro-magnetic.

7. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a size range capable of producing enhanced local fields when excited externally so that Raman scattering is increased.

8. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a size range capable of producing enhanced local fields when excited externally so that transitional phenomena are enhanced.

9. The nanoparticle-nanostructured material composite of embodiment 1, wherein said transitional phenomena comprise optical absorption, reflectance, fluorescence, ionization, field emission, charge separation, charge transfer and stimulated emission.

10. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a size range capable of producing enhanced local fields when excited externally so that photovoltaic conversion is increased.

11. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a spherical-like or an ellipsoidal-like configuration.

12. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a size range limited by the feature size of the nanostructured material.

13. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanostructured material comprises a thin film.

14. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise silver, gold, iron, palladium, platinum, or copper.

15. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles are mono-dispersed.

16. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanoparticles comprise a three-dimensional array.

17. The nanoparticle-nanostructured material composite of embodiment 1, wherein said nanostructured material comprises a void-column morphology having a plurality of rod-like units.

18. The nanoparticle-nanostructured material composite of embodiment 17, wherein said nanostructured material comprises pores disposed between the rod-like units, said pores limiting the size range of the nanoparticles.

19. A process for fabricating a nanoparticle-nanostructured material composite comprising:

a) preparing a nanostructured material; and

b) contacting the nanostructured material with a solution so that nanoparticles are synthesized on said material.

20. The process of embodiment 19, wherein said solution comprises a salt solution.

21. The process of embodiment 19, wherein said nanostructured material comprises a thin film.

22. The process of embodiment 19, wherein said nanostructured material comprises a void-column thin film having a plurality of rod-like units.

23. The process of embodiment 19, wherein said nanostructured material disperses the nanoparticles so that aggregation is minimized.

24. The process of embodiment 19 further comprising electrically biasing the nanostructured material.

25. The process of embodiment 20, wherein the salt solution comprises a copper sulfate, silver sulfate, silver nitrate, copper chloride, or gold chloride metal salt solution.

26. The process of embodiment 19, wherein the solution contains an analyte to be detected in connection with a molecular detection application.

27. The process of embodiment 19, wherein the nanoparticles comprise silver, gold, iron, palladium, platinum, or copper.

28. The process of embodiment 19, wherein said nanostructured material preparation step employs a physical vapor deposition technique, a chemical vapor deposition technique, an electrochemical etching technique, a stain etching technique or a high density plasma deposition technique.

29. A process for fabricating a nanoparticle-nanostructured material composite comprising:

a) preparing a nanostructured material having an interconnected void network; and

b) contacting the nanostructured material with a nanoparticle suspension so that particles are adsorbed on a surface of the material or are disposed throughout the material.

30. The process of embodiment 29 further comprising electrically biasing the nanostructured material.

31. The process of embodiment 29, wherein said nanostructured material comprises a thin film.

32. The process of embodiment 29, wherein said nanostructured material comprises a void column morphology having a plurality of rod like units.

33. The process of embodiment 29, wherein said nanostructured material disperses the nanoparticles so that aggregation is minimized.

34. The process of embodiment 29, wherein the particles comprise silver, gold, palladium, platinum, iron, or copper.

35. The process of embodiment 29, wherein said nanostructured material preparation step employs a physical vapor deposition technique, a chemical vapor deposition technique, an

electrochemical etching technique, a stain etching technique or a high density plasma deposition technique.

36. The process of embodiment 19 or 29 used to fabricate a charge separation device.

37. The process of embodiment 19 or 29 used to fabricate a photovoltaic device.

38. The process of embodiment 19 or 29 used to fabricate a Raman scattering sensor for molecular detection.

39. The process of embodiment 19 or 29 used to fabricate a surface plasmon sensor for molecular detection.

40. The process of embodiment 39, wherein said surface plasmon sensor comprises an optical reflectance sensing mechanism or an absorption sensing mechanism.

41. The process of embodiment 19 or 29 used to fabricate an optical absorption sensor for molecular detection.

42. The process of embodiment 19 or 29 used to fabricate a fluorescent device, fluorescence detection system or fluorescence enhancing apparatus.

43. The process of embodiment 19 or 29 used to fabricate an ionization device or sensor.

44. The process of embodiment 19 or 29 used to fabricate a stimulated emission device.

45. The process of embodiment 19 or 29 used to fabricate a catalyst.

46. The process of embodiment 19 or 29 used to fabricate a device capable of coupling electromagnetic radiation from one system to another.

47. The process of embodiment 19 or 29 used to fabricate an anti-reflection coating.

48. The process of embodiment 19 or 29 further comprising selectively patterning the nanoparticles on said nanostructured material.

49. The process of embodiment 48 used to fabricate an optical or magnetic information storage system.

50. The process of embodiment 48, wherein a dip pen lithography system is employed in connection with said selective patterning step.

51. A composition of matter formed by the process of embodiment 19 or 29.

52. An article of manufacture formed by the process of embodiment 19 or 29.

53. An article of manufacture comprising the nanoparticle-nanostructured material composite of embodiment 1.

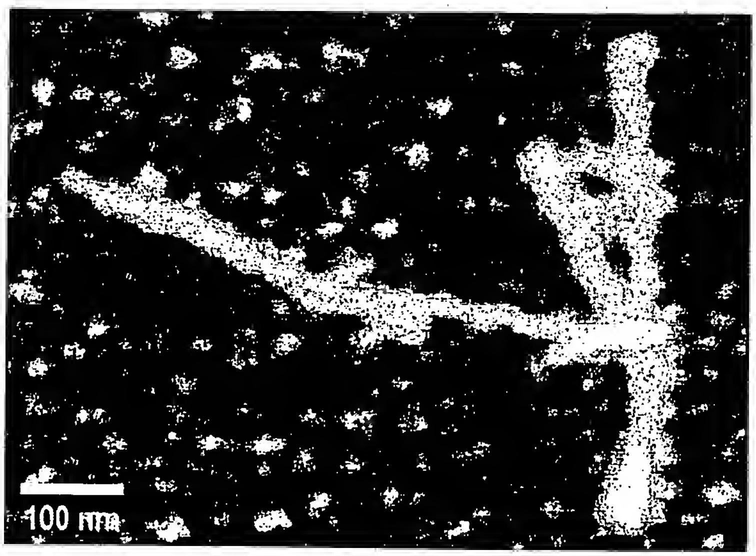


FIG 1. SEM micrograph of a nanostructured void-column Si film deposited as in Table I

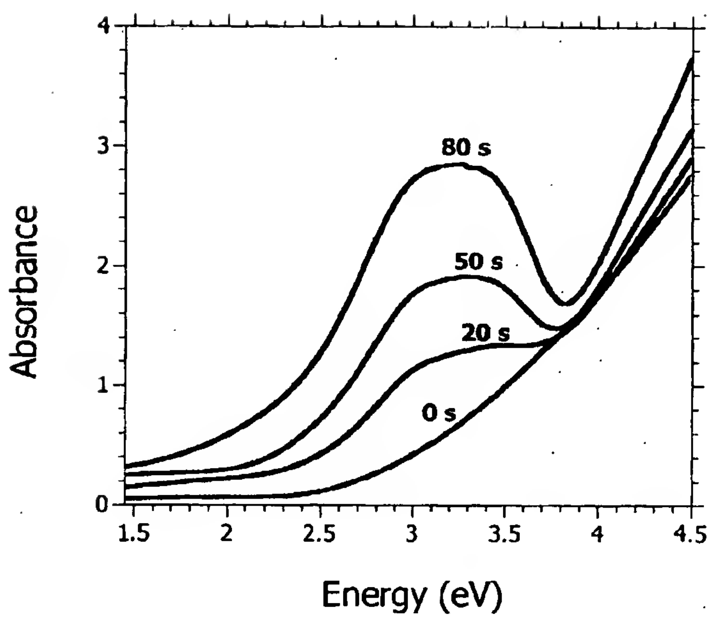


FIG 2. Time evolution of optical absorbance of void-column Si films immersed in 0.001 M Ag_2SO_4 solution.

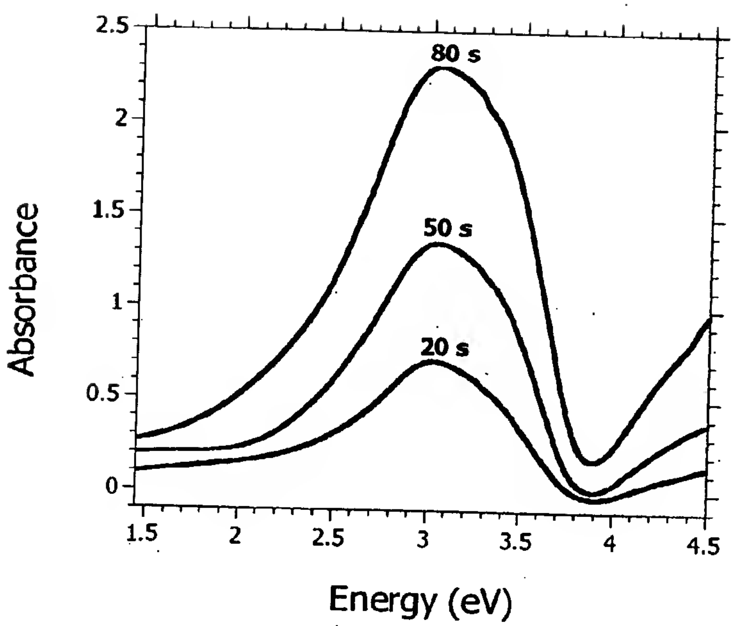


FIG 3. Surface plasmon absorption associated with Ag nanospheres synthesized on void-column Si films by immersion in 0.001 M Ag_2SO_4 solution for 20, 50 and 80 s.

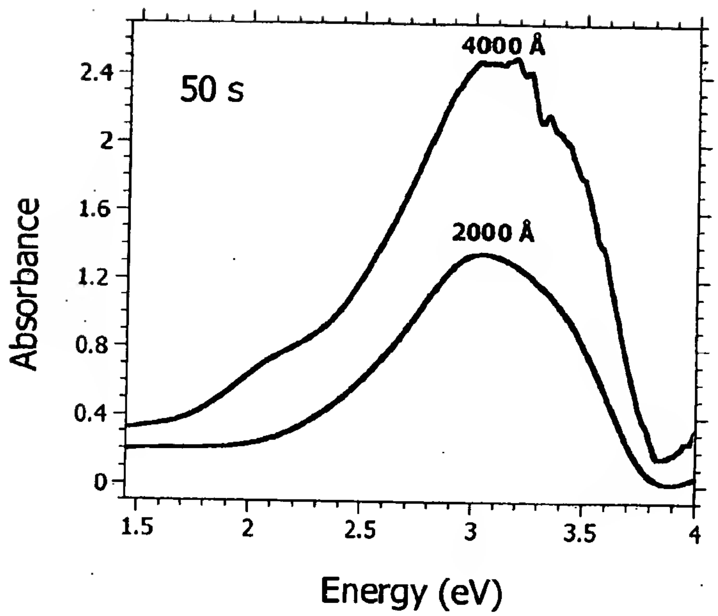


FIG 4. Impact of film thickness on surface plasmon absorption. Both films were immersed in 0.001 M Ag_2SO_4 solution for 50 s.

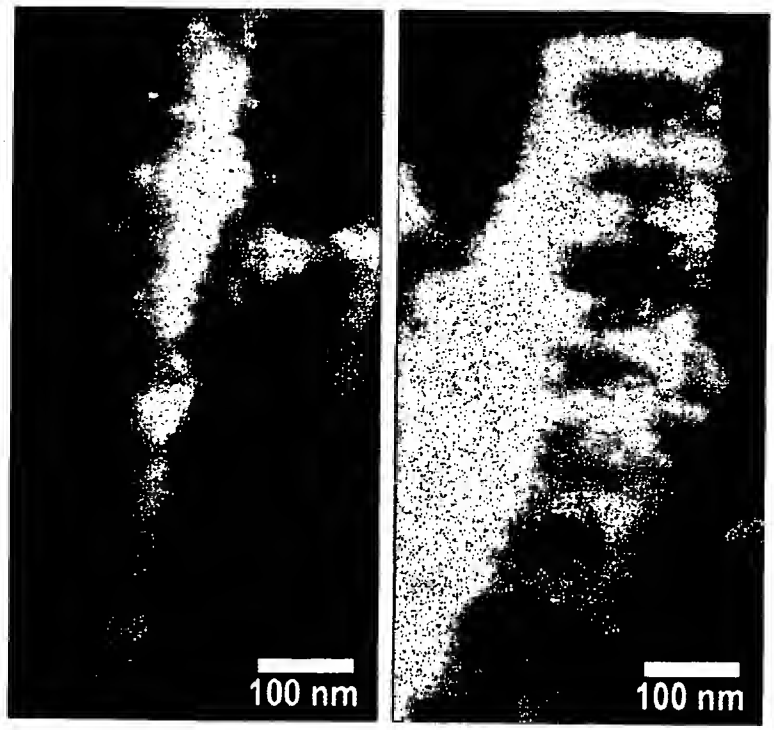


FIG. 5 Cleaved cross sections of a nanostructured void colum Si thin film immersed in in 0.001 M Ag_2SO_4 solution for 80 s. Ag nanoparticles are clearly seen to be synthesized inside the void network. This enables effective adsorption and immobilization of analyte molecules.

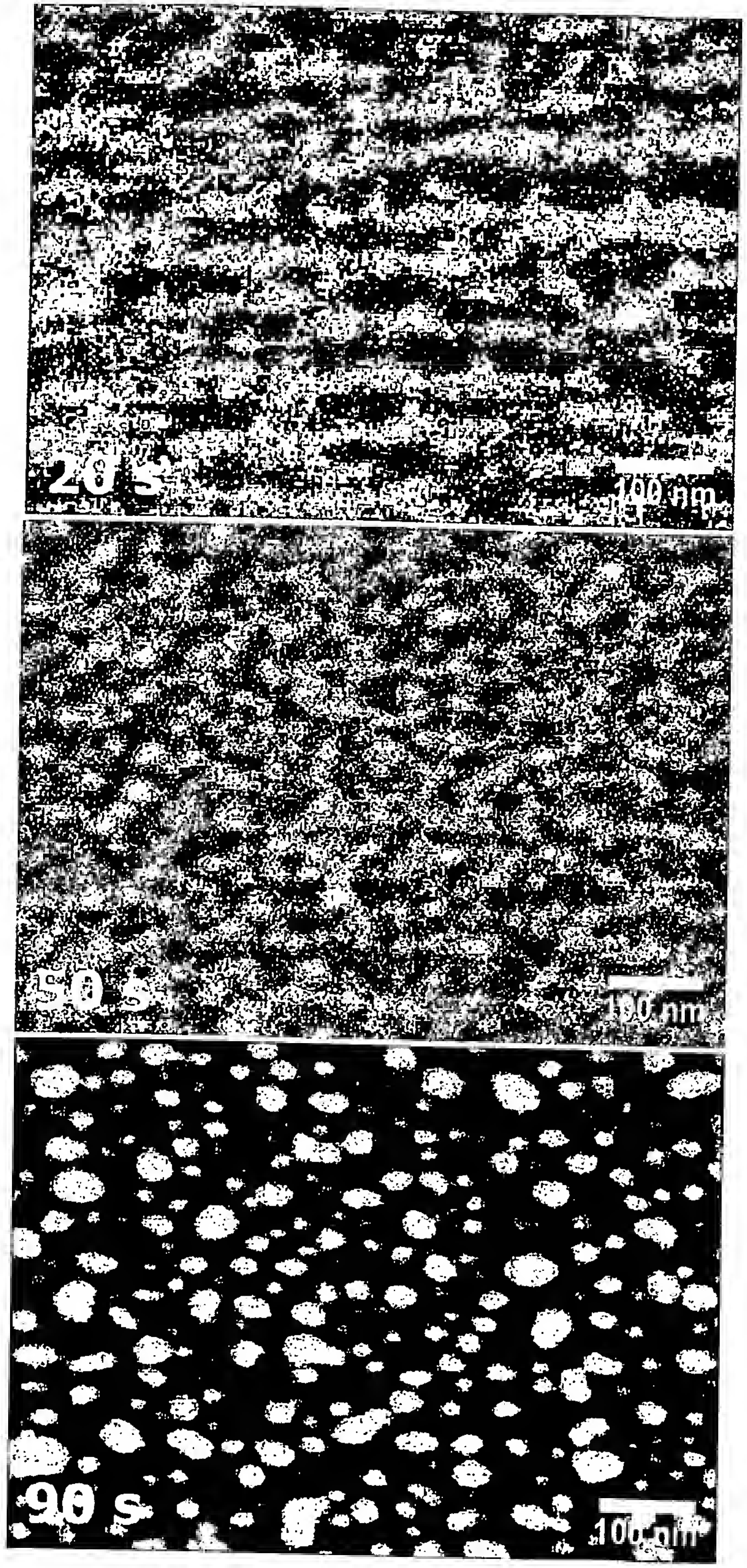


FIG 6. SEM micrographs of the top surface of nanostructured void-column Si films after 20, 50, and 90 s 0.001 M Ag_2SO_4 exposures.

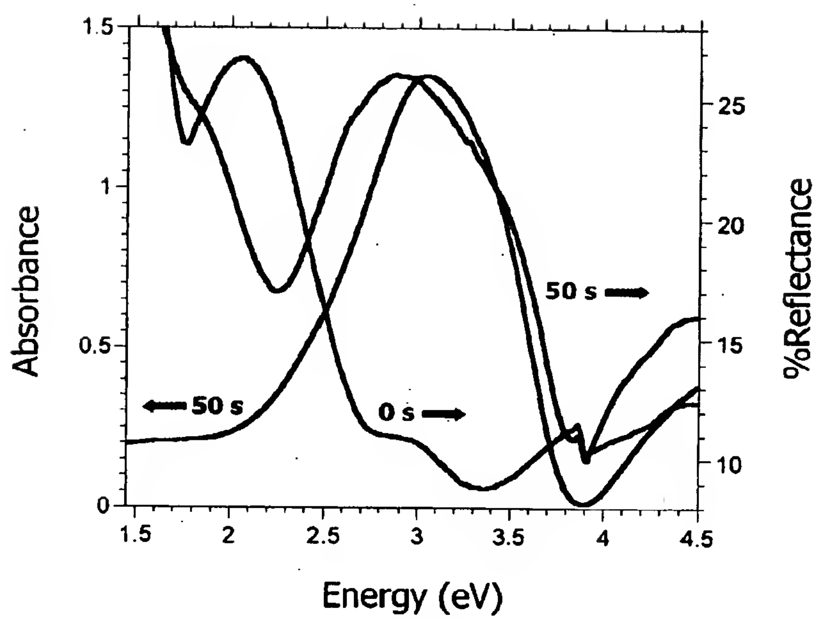


FIG 7. Reflectance of the void-column Si film that was coated with Ag nanoparticles for 50 s in the 0.001 M Ag_2SO_4 solution. Here the reflectance spectrum of an as deposited void-column Si film is also plotted. A pronounced reflectance band emerges due to the presence of Ag nanoparticles. The band has about the same peak location and width as the plasmon absorbtion band (also shown).

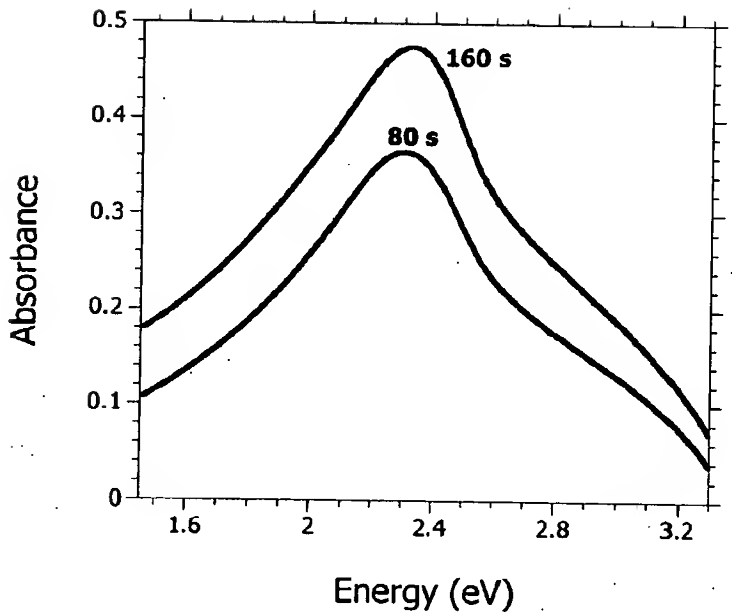


FIG 8. Surface plasmon absorption by Au nanoparticles synthesized on the surface of a void-column Si film by immersion in a commercial Au electroplating solution for 80 s and 160 s.

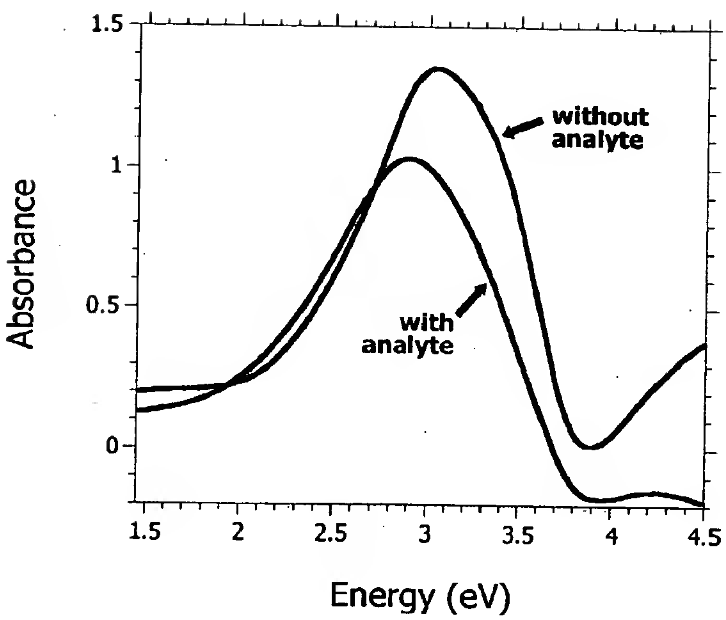


FIG 9. Demonstration of a SPR sensor. The analyte molecule is methyl sulfoxide. The nanostructured void-column Si film was coated with Ag nanoparticles by immersion in 0.001 M Ag_2SO_4 solution for 50 s. A red shift of the plasmon absorbtion occurs in response to the adsorption of the analyte onto the surface.

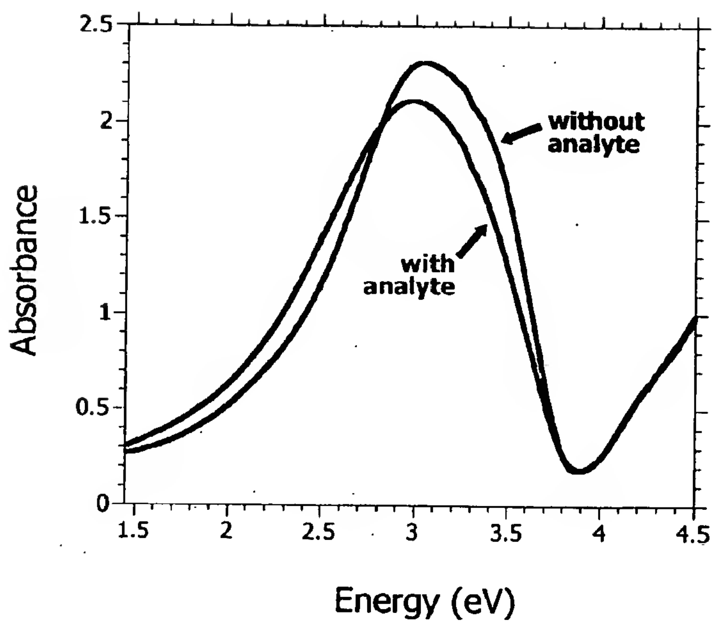


FIG 10. Demonstration of a SPR sensor. The analyte molecule is methyl sulfoxide. The nanostructured void-column Si film was coated with Ag nanoparticles by immersion in 0.001 M Ag_2SO_4 solution for 80 s. A red shift of the plasmon absorbtion occurs in response to the adsorption of the analyte onto the surface.

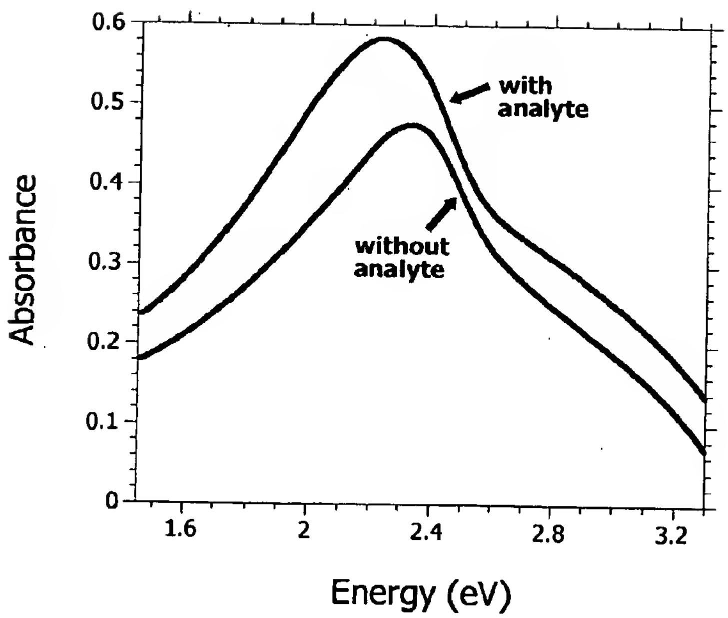
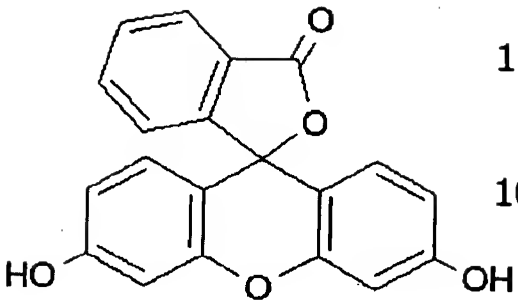


FIG 11. Demonstration of a SPR sensor. The analyte molecule is methyl sulfoxide. The nanostructured void-column Si film was coated with Au nanoparticles by immersion in a commercial electroplating gold solution for 160 s. A red shift of the plasmon absorbtion occurs in response to the adsorption of the analyte onto the surface.



Fluorescein

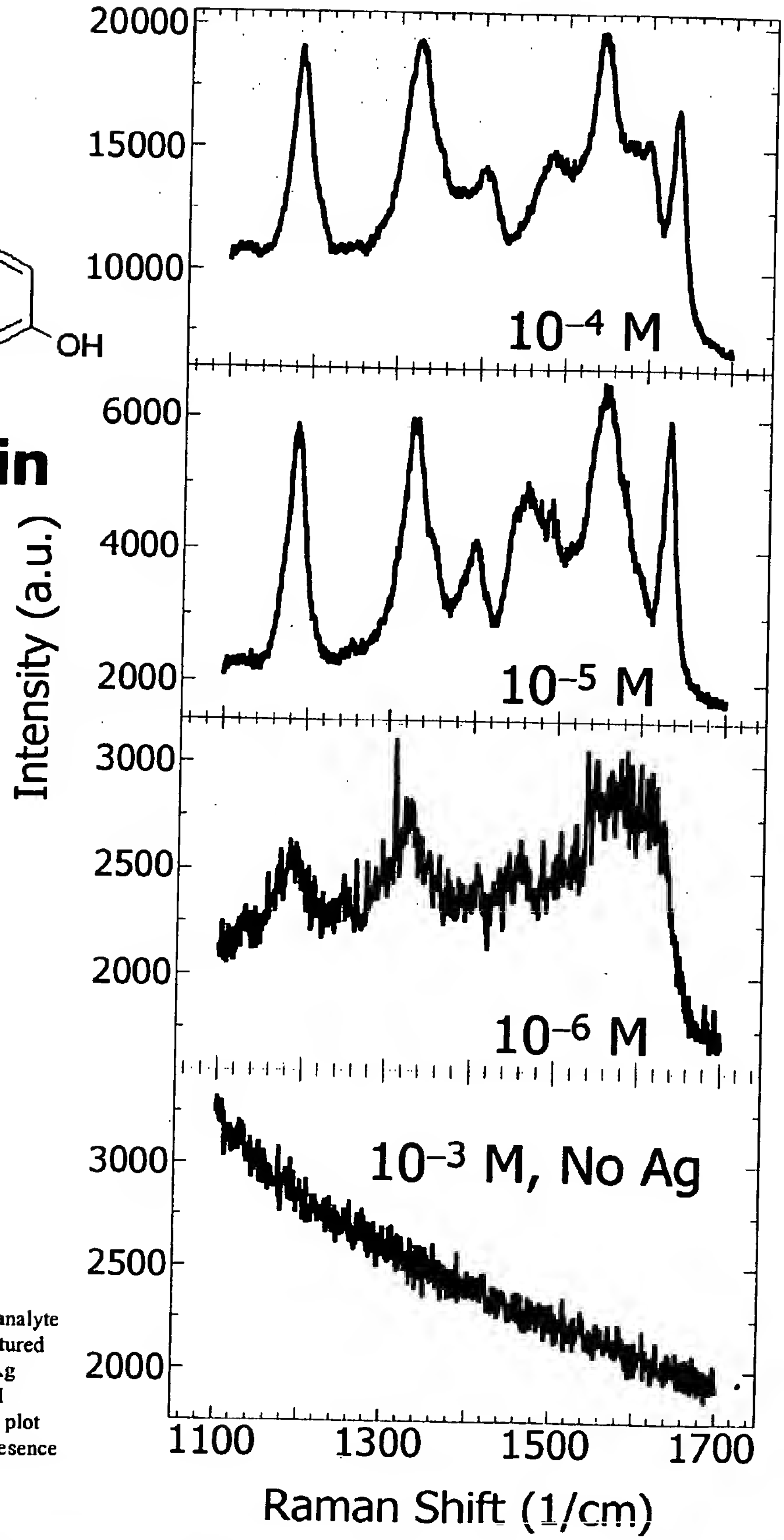


FIG 12. Demonstration of SERS. The analyte molecule is fluorescein. The nanostructured void-column Si film was coated with Ag nanoparticles by immersion in 0.001 M Ag_2SO_4 solution for 110 s. The bottom plot shows the Raman signal without the presence of Ag nanoparticles.

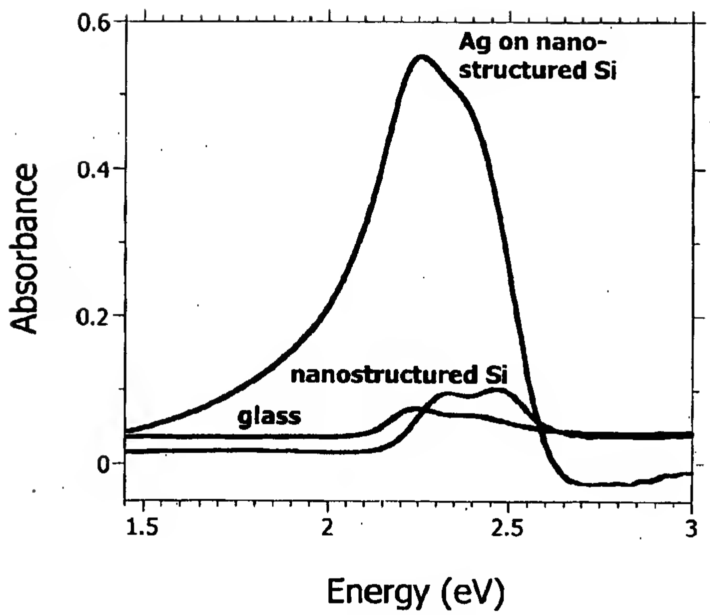


FIG 13. Optical absorption spectra of rhodamine spun on three different substrates at 1000 rpm for 10 s (0.001 M dissolved in cyclohexanone). "Ag on nano-structured Si" substrate was prepared by immersion of a nanostructured void-column Si film in 0.001 M Ag_2SO_4 solution for 90 s. The rhodamine spectrum for each case was obtained by subtracting the substrate absorbance from substrate+rhodamine absorbance. Enhancement in optical absorption is evident in the presence of Ag nanoparticles. A blueshift of absorption is also seen when it is spun on nanostructured Si.

[redacted]

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/001696

International filing date: 21 June 2004 (21.06.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/441,743
Filing date: 21 January 2003 (21.01.2003)

Date of receipt at the International Bureau: 10 September 2004 (10.09.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)